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Energetics of HMX-Based Composite Modified Double-Base Propellant Combustion

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The burning rate and gas-phase structure of HMX-based composite modified double-base (CMDB) propellants were studied to characterize the combustion process as a function of the mass fraction of NO_2, $\xi(NO_2)$, within the propellants. The burning rate decreased even though $\xi(NO_2)$ was increased by the increase of the mass fraction of HMX. The adiabatic flame temperature was increased by the increased $\xi(NO_2)$, but the temperature in the dark zone and the temperature gradient in the fizz zone just above the burning surface were decreased. Based on the observed relationship between burning rate and pressure, a generalized burning rate equation of HMX-CMDB propellants was obtained as a function of $\xi(NO_2)$.

Introduction

INASMUCH as the energy contained within double-base propellants is limited because of the limited energies of nitrocellulose (NC) and nitroglycerin (NG), which are major ingredients of double-base propellants, the addition of energetic crystalline materials such as HMX and RDX increases the combustion temperature and specific impulse. These types of double-base propellants are the so-called nitramine-based composite modified double-base (CMDB) propellants. HMX and RDX are stoichiometrically balanced materials and produce high-temperature combustion gases, and thus the addition of these nitramine particles within a double-base propellant increases the combustion temperature and specific impulse. However, the burning mode of these nitramine particles is different from that of double-base propellants. The burning rate of nitramine-CMDB propellants appears to be different from that of the double-base propellant that is used as a base matrix.

There have been numerous theoretical and experimental studies on double-base propellants[1–10] and HMX,[11–19] and their combustion mode and burning rate characteristics are understood. However, limited studies on HMX-CMDB propellants have been conducted.[20–24] Kubota and Masamoto proposed a combustion model of HMX-CMDB propellants to gain the parameters that effect on the burning rate vs pressure relationship.[25] The decomposed gases produced by HMX particles and its base matrix (double-base propellant) diffuse, mix together, and produce relatively homogeneous gases on and above the burning surface of the HMX-CMDB propellant. The burning rate of HMX-CMDB propellants appears to be less dependent on the particle size of mixed HMX.[25]

It has been reported that the burning rate of a double-base propellant increases with increasing energy contained in the unit mass of propellant at a constant pressure.[8,10] This is caused by the increased reaction rate in the gas phase and the increased heat release at the burning surface. Because the primary ingredients of double-base propellants are nitrate esters such as NC and NG, the energy of a double-base propellant is represented by the number of O–NO_2 chemical bonds contained within the unit mass of propellant. The breaking of O–NO_2 bonds produces NO_2, aldehydes, and C–H–O species. The NO_2 acts as an oxidizer component and reacts with the aldehydes and C–H–O species, which act as fuel components.[1–8] This reaction is highly exothermic, and the burning rate of double-base propellants is determined by this reaction process.[10,19,20] Thus, the burning rate of double-base propellants is correlated by the mass fraction of NO_2, $\xi(NO_2)$ (Ref. 10).

The chemical structure of HMX is $(CH_2)_4(N–NO_2)_4$, and the decomposed fragments of N–NO_2 bonds produce nitrogen oxides such as NO_2, NO, and oxide radicals. These nitrogen oxides are considered to act as oxidizer components, and the remaining C–H–O fragments act as fuel components. These oxidizer and fuel components react to produce high-temperature combustion products in the gas phase.[20,25] Because the $\xi(NO_2)$ contained within the unit mass of HMX is higher than that of double-base propellants, the gas-phase reaction would be enhanced by the addition of HMX.

The addition of HMX particles changes not only the energetics but also the combustion mode of double-base propellants. The physical structure of double-base propellants is highly homogeneous due to the gelatinized nature of the mixture of NC, NG, and stabilizers. The mixture of HMX crystalline particles makes not only the physical structure of the double-base propellant used as its base matrix heterogeneous, but also the gas-phase structure heterogeneous.[1] Yano and Kubota [22,23] and Kubota and Okuhara[24] reported that the burning rate of double-base propellants is reduced by the addition of HMX due to the reduced heat release at the burning surface and the reaction rate in the gas phase. The heat release of the decomposition of the HMX particles occurs relatively independently from the decomposition of the base matrix used. The overall heat release at the burning surface of HMX-CMDB propellants is represented by[25]

$$Q_{s,\mathrm{CMDB}} = \xi_{(\mathrm{HMX})} Q_{s,\mathrm{HMX}} + \left(1 - \xi_{(\mathrm{HMX})}\right) Q_{s,\mathrm{DB}} \tag{1}$$

where $Q_{s,\mathrm{CMDB}}$, $Q_{s,\mathrm{HMX}}$, and $Q_{s,\mathrm{DB}}$ are the heat release at the burning surface of the unit mass of HMX-CMDB propellants, HMX particles, and the base matrix, respectively. Equation (1) indicates that the heat release of HMX-CMDB propellant appears to be the mass-averaged heat release of HMX particles and the base matrix. The heat release values determined by the combustion model are $Q_{s,\mathrm{HMX}} = 209$ kJ/kg and $Q_{s,\mathrm{DB}} = 418$ kJ/kg (Ref. 1).

In this study, attention has been given to the total concentration of NO_2, $\xi(NO_2)$, contained within HMX-CMDB propellants in order to correlate the burning rate and the energy contained within the unit mass of propellant. The combustion characteristics, such as the burning rate and temperatures in the gas phase, are measured to gain information on the effect of $\xi(NO_2)$ enhanced by the addition of HMX particles.

Experimental

Physicochemical Properties of HMX-CMDB Propellants Used

The double-base propellant used as a base matrix of this study consisted of ξ(NC: 0.25), ξ(NG: 0.65), and ξ(DEP: 0.10), and the heat of explosion was 4.763 MJ/kg. The nitrogen concentration of nitrocellulose used was 12.2%, and the mass fraction of NO_2 contained within the base matrix was $\xi(NO_2$: 0.496). Three types of HMX-CMDB propellants were formulated: the mass fractions of HMX,

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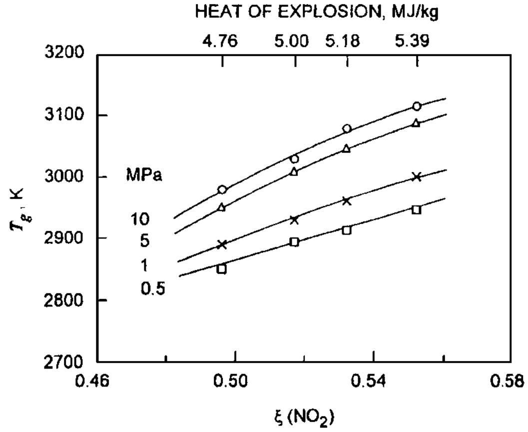

Fig. 1 Relationship of the adiabatic flame temperature T_d, the heat of explosion, and the mass fraction of NO_2, $\xi(NO_2)$, contained within the unit mass of HMX-CMDB propellants tested.

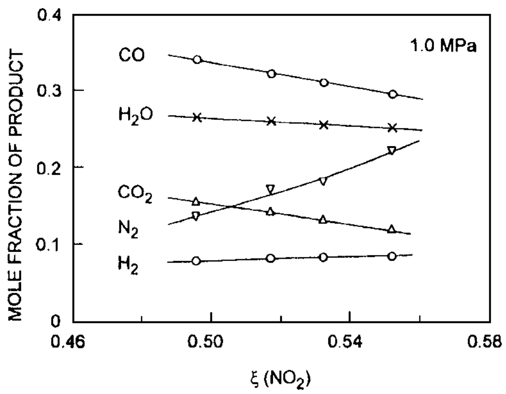

Fig. 2 Mole fraction of combustion products as a function of $\xi(NO_2)$ showing that the mole fraction of N_2 increases as $\xi(NO_2)$ increases.

ξ(HMX), used were 0.167, 0.286, and 0.444. Figure 1 shows the adiabatic flame temperature T_g of HMX-CMDB propellants tested as a function of $\xi(NO_2)$ at thermal equilibrium conditions. It is shown that T_g increases with increasing $\xi(NO_2)$, that is, $\xi(NO_2)$ increases with increasing ξ(HMX). The chemical abbreviations of NC, NG, and DEP are nitrocellulose, nitroglycerin, and diethylphthalate, respectively.

Figure 2 shows the relationship between $\xi(NO_2)$ and the mole fraction of combustion products at 10 MPa. Though the mole fraction of CO, H_2O, and CO_2 decreases with increasing $\xi(NO_2)$, the mole fraction of N_2 increases with $\xi(NO_2)$. The mole fraction of H_2 remains relatively unchanged in the range of examined, $\xi(\text{HMX}) = 0.0 \sim 0.444$.

The HMX particles used to formulate HMX-CMDB propellants are β crystal shape, and the mean particle size is 20 μm in diameter. The heat of explosion of each propellant determined theoretically is also shown in Fig. 1. The heat of explosion increases as $\xi(NO_2)$ increases, and the flame temperature also increases.

Burning Rate and Temperature Measurements

The burning rate of the propellants were measured by a chimney type of strand burner that was pressured with nitrogen gas. The size of propellant strands was 7×7 mm in cross section and 70 mm in length, and the side of the strands were coated with an inhibitor. The burning rate was obtained from visual records of a high-speed video camera taken through the transparent window that was attached on the side of the strand burner.

The temperature in the combustion wave during propellant burning was measured using microthermocouples that were embedded within the propellant strands. Two types of thermocouples were used: 5.0 and 25 μm in diameter made of Pt–Pt 10% Rh wires. The measurement techniques are described elsewhere.[7–10]

Results and Discussion

Burning Rate Characteristics

Figure 3 shows the relationship of burning rate and $\xi(NO_2)$ at different pressures. The burning rate decreases linearly as $\xi(NO_2)$ increases at a constant pressure in $\xi(NO_2)$ vs log (burning rate) plot. Thus, the burning rate is

$$r = cp^m \exp[a\xi(NO_2)] \tag{2}$$

where r is burning rate (millimeter per second), a is a constant, p is pressure (megapascal), m is a pressure exponent, and c is a constant (millimeter per second), when the initial propellant temperature T_0 is given. As shown in Fig. 4, m increases slightly as $\xi(NO_2)$ increases, but remains unchanged when pressure is changed within the range of pressures $0.5 \sim 5.0$ MPa tested. Using the results shown in Figs. 3 and 4, the parameters of the burning rate equation (2) are given as $a = -5.62$ and $c = 38.3$ mm/s at $T_0 = 293$ K.

Because the pressure exponent depends highly on the reaction process in the gas phase, the results indicate that the fundamental reaction pathway in the gas phase of double-base propellants remains relatively unchanged by the addition of HMX particles. However, note that the burning rate of double-base propellants increases as $\xi(NO_2)$ increases at a constant pressure as demonstrated by Aoki and Kubota.[10]

Thermal Structure in Combustion Wave

The gas-phase structure of the propellants tested appears to be two-staged combustion with and without of HMX addition. A luminous flame stands above the burning surface, and the flame standoff distance decreases as pressure increases. The region between the burning surface and the flame front of the luminous flame zone is the so-called dark zone for double-base propellants.[1–10] The flame standoff distance (the dark zone length) decreases with increasing ξ(HMX) at a constant pressure. These results have been reported

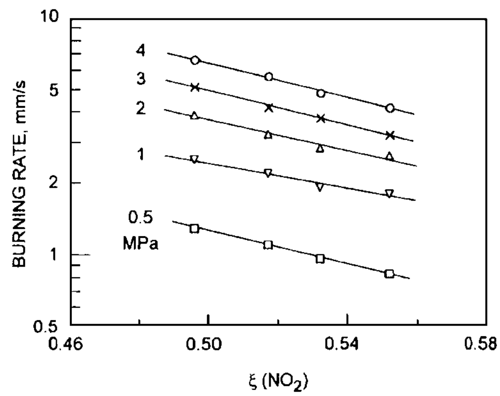

Fig. 3 Measured burning rate vs $\xi(NO_2)$ at various burning pressures showing that the burning rate decreases as $\xi(NO_2)$ increases.

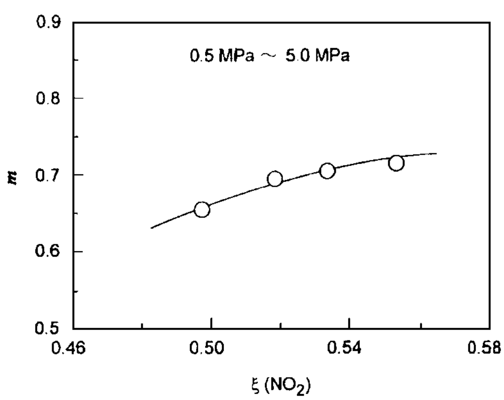

Fig. 4 Pressure exponent of burning rate vs $\xi(NO_2)$ showing that the pressure exponent increases slightly as $\xi(NO_2)$ increases.

previously.[22–24] Note that the homogeneous nature in the gas phase of a double-base propellants remains unchanged even when crystalline HMX particles are mixed within a double-base propellant.

To determine the temperature profiles in the combustion wave and the heat flux transferred back from the gas phase to the burning surface, microthermocouples (25- and 2.5-μm wire diameter) were imbedded within the propellant strands. The thermal structure appears to remain relatively unchanged by the addition of HMX (Refs. 22–24). The temperature increases from the initial temperature of propellant, T_0, and reaches its burning surface temperature T_s. A rapid temperature rise occurs above the burning surface and reaches T_d, the temperature in the dark zone. The temperature becomes relatively unchanged up to a certain distance from the burning surface and increases again farther downstream in the gas phase. Unfortunately, no measured data of the temperature in the luminous flame zone were available because the temperature exceeded the upper limit of the microthermocouple measurements (~1800 K) used in this study. The thermal structure of HMX-CMDB propellants appears to be similar to that of double-base propellants.

Figure 5 shows the relationship of T_g vs T_d at different burning pressures. It is shown that T_d decreases as T_g increases in the pressure range tested. This indicates that the addition of HMX decreases T_d, which is the temperature of an intermediate reaction zone, that is, the dark zone. On the other hand, T_d increases with increasing pressure at a constant $\xi(NO_2)$. The burning rate is correlated with a straight line in a log r vs T_d plot, as shown in Fig. 6. However, the burning rate increases with increasing T_d at a constant $\xi(NO_2)$, that is, the burning rate increases as pressure increases. Figure 7 shows the burning rate as a function the adiabatic flame temperatureT_g as a function of pressure. The burning rate decreases as T_g increases, which indicates the burning rate decreases as the energy contained within the unit mass of propellant increases. Similar results have been reported by Yano and Kubota,[22,23] Kubota and Okuhara,[24] and Kubota and Masamoto.[25]

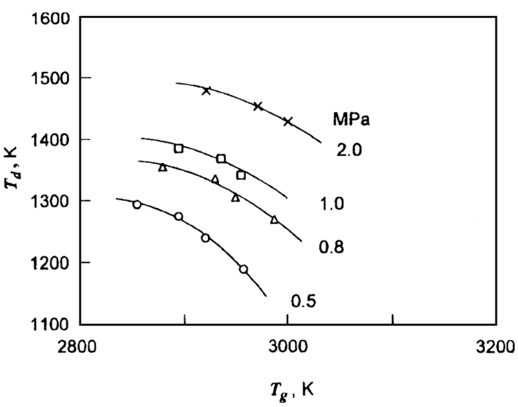

Fig. 5 Dark zone temperature T_d decreases as adiabatic flame temperature T_g decreases.

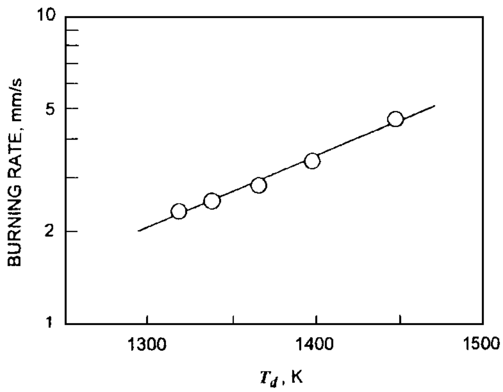

Fig. 6 Burning rate increases as dark zone temperature increases.

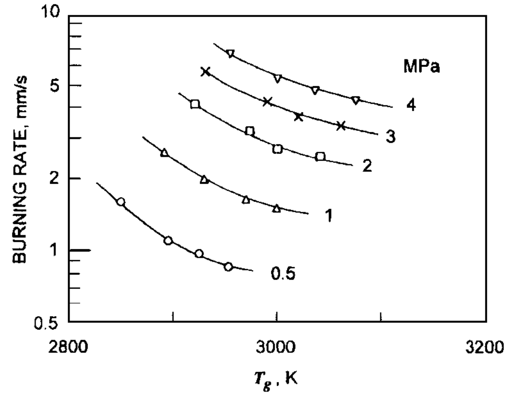

Fig. 7 Burning rate decreases as adiabatic flame temperature increases, that is, burning rate decreases as $\xi(NO_2)$ increases.

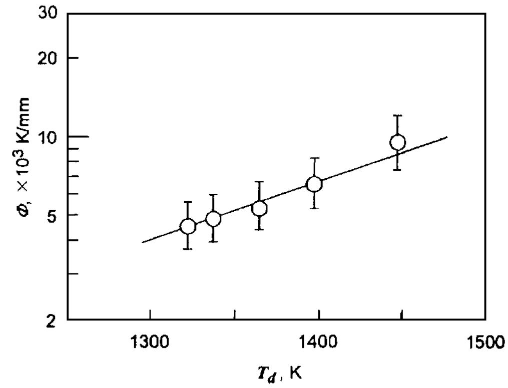

Fig. 8 Temperature gradient in the fizz zone, Φ, increases as dark zone temperature decreases, that is, temperature gradient increases as $\xi(NO_2)$ decreases.

In general, the burning rate of solid propellants is determined by the heat flux transferred back from the gas phase to the solid phase and the heat flux generated at the burning surface.[20] The temperature gradient in the fizz zone, $\Phi = (\mathrm{d}T/\mathrm{d}x)_f$, that is, the temperature gradient just above the burning surface, is an important parameter to understand the heat feedback process from the gas phase to the burning surface, where T is temperature, x is distance, and f is the fizz zone. Though the output signals of temperature measurements indicated that the temperature in the fizz zone increased rapidly with small fluctuations, the time-averaged profile appeared to be similar to that of double-base propellants. As shown in Fig. 8, the measured Φ increases linearly in log Φ vs T_d plot. It should be noted that T_d decreases with increasing T_g, that is, $\xi(NO_2)$, at a constant pressure, as shown in Fig. 5. Furthermore, Φ also decreases as $\xi(NO_2)$ increases, and thus, the burning rate decreases as $\xi(NO_2)$, that is, ξ(HMX), increases at a constant pressure, as shown in Fig. 3.

Conclusions

The burning rate of HMX-CMDB propellants has been represented by Eq. (2) as a function of $\xi(NO_2)$: The burning rate decreases as $\xi(NO_2)$ increases at a constant pressure. However, the burning rate increases as pressure increases at a constant $\xi(NO_2)$. The examination of the gas-phase structure by microthermocouples revealed that the temperature in the dark zone and the temperature gradient in the fizz zone decrease as $\xi(NO_2)$ increases. Noted that the burning rate of double-base propellants increases as $\xi(NO_2)$ increases, as reported previously. This is caused by the difference of decomposition and heat release mechanisms between HMX composed of an N–NO_2 bond and double-base propellants composed of an O–NO_2 bond.

The observed burning rate characteristics are understood through the results of the gas-phase measurements conducted in this study and the heat release at the burning surface represented by a simplified relationship of Eq. (1), that is, the decreased burning rate is caused by the lowered heat release at the burning surface and the lowered reaction rate in the fizz zone when HMX particles are added into double-base propellants. However, further extended experimental studies are needed to elucidate the detailed chemical reaction process at the burning surface and in the fizz zone.

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